

## LA-UR-21-23989

Approved for public release; distribution is unlimited.

Title: Protocols for Uranium Carbon Analysis

Author(s): Tubesing, Philip K.  
Korzekwa, Deniece Rochelle  
Bremser, Julie K

Intended for: Report

Issued: 2021-05-19 (rev.1)

---

**Disclaimer:**

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

# Protocols for Uranium Carbon Analysis

Philip K. Tubesing, Deniece R. Korzekwa, Julie K. Bremser  
Los Alamos National Laboratory, Sigma Complex

In 1998, MST-6 (now SIGMA) installed a Horiba EMIA-8200 Carbon/Sulfur analyzer to provide the ability to perform in-house chemical analysis on a variety of materials including uranium. While many of the results and procedures were detailed in program files, no compiled record of the overall analytic process was ever published. This retrospective utilizes existing logbooks, operator interviews, instrument manuals, and notes to catalog what is known about the past procedures and protocols for carbon analysis that were established and present the data informing those decisions.

## Table of Contents

<b><i>Established Protocols for Carbon Analysis .....</i></b>	<b><i>2</i></b>
<b><i>Sample Size .....</i></b>	<b><i>2</i></b>
<b><i>Flux .....</i></b>	<b><i>2</i></b>
<b><i>Sample Preparation .....</i></b>	<b><i>2</i></b>
<b><i>Background .....</i></b>	<b><i>3</i></b>
<b><i>Sample Size .....</i></b>	<b><i>4</i></b>
Low-carbon Uranium (FSDrum-16) .....	4
High-Carbon Uranium (98C-452) .....	5
Natural Uranium Round Robin .....	6
Unknown Steel Rod .....	9
Granular Steel Standard.....	10
Additional Data Sets Not Used .....	12
<b><i>Flux .....</i></b>	<b><i>13</i></b>
<b><i>Sample Preparation.....</i></b>	<b><i>14</i></b>
<b><i>Sample Morphology .....</i></b>	<b><i>16</i></b>

## Established Protocols for Carbon Analysis

### Sample Size

- We established 1g as the standard sample size for solid, monolithic samples of uranium and most other materials, based upon manufacturer's recommendations and several sample size studies.
- We established 0.5g (500mg) as the minimum sample size we felt provided consistent results, based upon several sample size studies.

### Flux

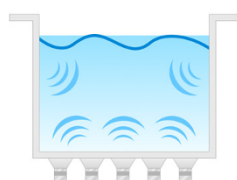
- We established the following flux recipe standard based upon the manufacturer's operating manual and some experimental testing.

1.5g W (tungsten) + 0.3g Sn (tin) + sample

### Sample Preparation

- We established the following sample preparation method based upon manufacturer's recommendations, experience at other facilities performing uranium carbon analysis, and our own evaluation tests.

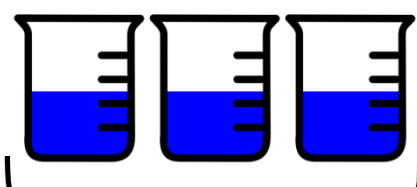
1. Ultrasonic bath in soapy water	60 sec
2. 10% dilute nitric acid	90 sec
3. De-ionized water rinse	20 sec
4. De-ionized water rinse	20 sec
5. De-ionized water rinse	20 sec
6. Acetone rinse	5-10 sec
7. Dry with "warm wind"	Visual check
8. Run analysis	As soon as possible



Soapy Water  
Ultrasonic bath  
60 sec



10% Dilute  
Nitric Acid  
90 sec <sup>1</sup>



3-Step De-Ionized  
Water Rinse Cascade  
20 sec each



Acetone  
Rinse  
5-10 sec <sup>2</sup>



Dry with  
"Warm Wind" <sup>3</sup>

## Background

In 1995-96, a GPP construction project paid for renovation of SM-66 G105 from a single, large, high-bay lab to a 2-story, multi-room characterization suite. While Sigma has a long history of metallurgical and physical characterization equipment, its chemical characterization capability needed to be upgraded and expanded. Following completion of the renovation, Sigma added or upgraded equipment for hydrogen, oxygen-nitrogen, GC/MS, particle/powder size, and carbon-sulfur analyses. At the time, we had limited direct experience with some of these, particularly the elemental analyzers.

As part of this capability expansion, we purchased a Horiba EMIA-8200 Carbon/sulfur analyzer in late 1997. The equipment was installed at Sigma 1/27-2/2, 1998. Over the balance of that fiscal year, we ran ~1000 samples through the analyzer to;

- 1) become proficient in the use and understanding of the equipment,
- 2) establish protocols for future measurements, and
- 3) perform analysis on samples for programmatic efforts.

During this time, most of the data were collected and reported to the individual programs being supported. We had intended to make a compilation report of our experiences and decisions, but that was never completed. This is an attempt to go back and catalog the history, report the protocols established, and present reasoning behind our decisions.

The three main protocols we established for uranium carbon analysis were;

- 1) standard and minimum sample sizes,
- 2) flux recipe, and
- 3) sample cleaning method.

Since monolithic solid samples were more easily available to us than they are today, we did not do adequate survey of sample morphology (solid, chips, powders)<sup>1</sup> to evaluate potential variations in analysis results as a function of sample form. We suggest some investigation into this may be useful.

While this analytic equipment is capable of measuring sulfur in addition to the carbon, there was not a significant programmatic driver for us to measure sulfur as part of normal analysis and reporting. In many cases, sulfur results are recorded in the log book, but not reported or used in any meaningful way.

---

<sup>1</sup> There are some results in Horiba EMIA-8400 log book #1, pages 8-9, 13-14, 93, that indicate evaluating chip samples. There is also one page of hand-written notes with results of cleaning and aging chips.

## Sample Size

- We established **1g** as the standard sample size for solid, monolithic samples of uranium and most other materials, based upon manufacturer's recommendations and several sample size studies.
- We established **0.5g (500mg)** as the minimum sample size we felt provided consistent results, based upon several sample size studies.

There are five sample size studies recorded in the log book, three using uranium and two using steel, we used to establish and confirm the use of this sample size range. The results of each study show that there is significant departure from the average carbon value and expansion of the standard deviation with sample sizes below 400-500mg. We present the results for each of the sample size studies below. We decided that we felt comfortable using 500mg or larger samples and established that as our lower limit.

Nearly all of the samples we used for uranium carbon analysis were cut from rods or pins that were machined from the initial feed stock. We found that 3mm diameter was about the maximum size we could hand cut with snips, electrician's pliers, or small bolt cutters in the G105 hood. Some samples were also cut on a benchtop metallurgical saw in the foundry.

### Low-carbon Uranium (FSDrum-16)

We used Feedstock Drum 16 (FSDrum-16) as a low-carbon depleted uranium reference material to verify low-carbon results. There are approximately 100 FSDrum-16 samples recorded overall in the log book. The consolidated value of all 1g FSDrum-16 samples is

FSDrum-16 (all 1g samples) <sup>2</sup>	ppmC
Average Carbon Value	57.4
Standard Deviation	17.9

We also used FSDrum-16 for a sample size study. Generally, we would run 10 samples at each size for materials we had not measured previously and for which we had adequate material for all the samples. As we gained experience with and feel for some of the materials, or had limited material supply, we would sometimes reduce this to 4 or 5.

FSDrum-16 Nominal Sample Size (mg)	Average Carbon (ppmC)	StDev
1000	62.1	9.4
500	47.2	21.0
250	77.7	32.7

---

<sup>2</sup> Pages 38, 41-42, 46-48, 50, 52, 138, 151 of Horiba EMIA-8400 log book #1

When we plotted these results (Figure 1), we saw that the 500mg sample average and deviation overlaid the overall FSDrum-16 average of 57.5ppmC, but the 250mg sample data was significantly higher and wider than our overall values. All four sample sets discussed in this section using solid sample forms exhibit a similar trend.

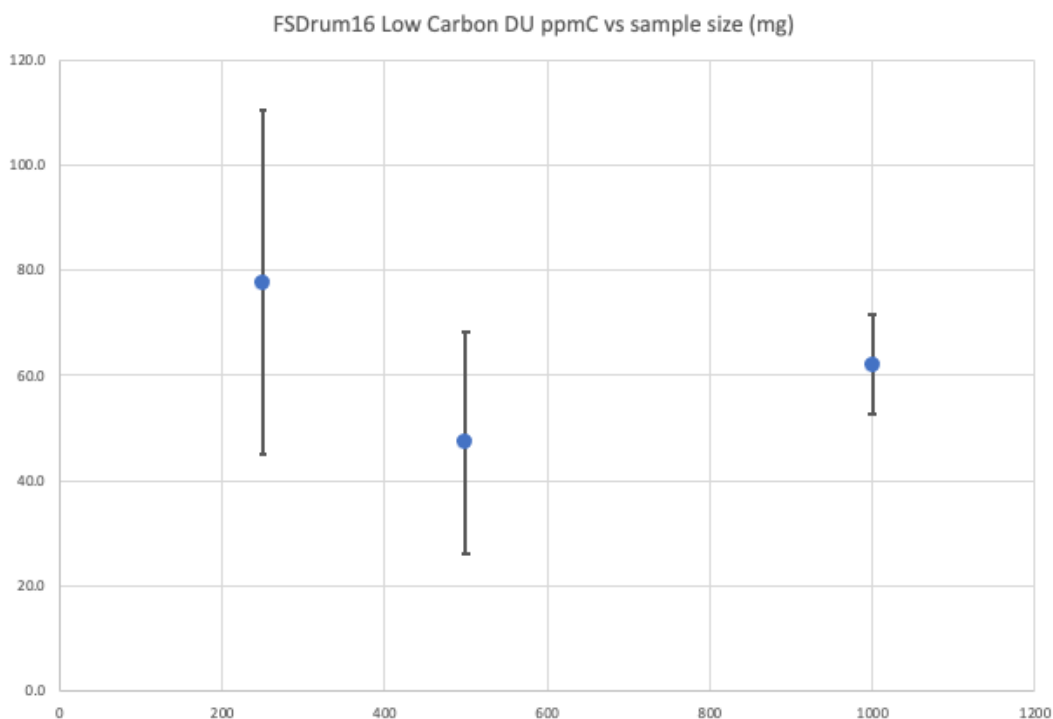


Figure 1: Low-carbon DU FSDrum-16 carbon content as a function of sample size

### High-Carbon Uranium (98C-452)

We used samples from casting 98C-452<sup>3</sup> to determine if there was any effect of high carbon level feedstock on the sample size study done on FSDrum-16. There were 10 samples run at each nominal mass.

98C-452 Nominal Sample Size (mg)	Average Carbon (ppmC)	StDev
1000	304.1	21.1
500	307.7	102.7
250	377.8	82.2
100	433.5	26.0

<sup>3</sup> Pages 145-146

We can see that these results show a pattern similar(Figure 2) to the low-carbon uranium results of a shift in average values and some expansion of the standard deviation.

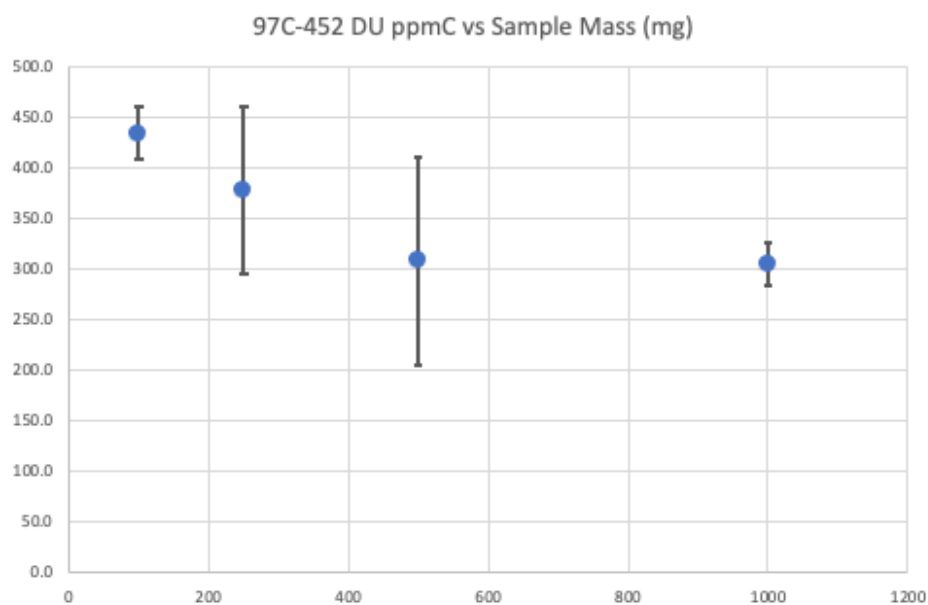


Figure 2: High-carbon DU 98C-452 carbon content as a function of sample size

### Natural Uranium Round Robin

As part of a DOE-wide effort to understand uranium carbon analysis, Lawrence Livermore led a carbon analysis round robin using natural uranium rods as the feedstock. Our recollection is that a number of rods were gang cast and distributed to LLNL, LANL, Y-12, MSC<sup>4</sup>, AeroJet<sup>5</sup>, and perhaps StarMet<sup>6</sup> for carbon analysis. Los Alamos received rods A3, B1, C15, E11, D13, and F9.<sup>7</sup> We were unable to locate any final reports from the round robin study. This is the most extensive sample size study we performed on uranium.

Natural Uranium Round Robin Lots	Average Carbon (ppmC)	StDev
RR-A3	56.9	3.0
RR-B1	45.5	17.1
RR-C15	56.5	6.1
RR-D13	47.9	12.6
RR-E11	103.9	32.6
RR-F9	53.5	17.0

<sup>4</sup> Manufacturing Sciences Corporation in Oak Ridge TN

<sup>5</sup> AeroJet (now AeroJet Rocketdyne) maintains uranium fabrication facilities outside Jonesborough TN

<sup>6</sup> Carolina Metals, subsequently purchased by StarMet, operated a uranium conversion facility outside Barnwell SC

<sup>7</sup> Pages 112-118

We performed sample size evaluations of two lots from the round robin material, D13 and F9. Lot F9 shows results very similar to FSDrum-16 and 98C-452. The 500mg samples have a very similar average, the average value of the 100mg samples is higher than the larger sample sizes and has a larger standard deviation.

RR-F9 Nominal Sample size (mg)	Average Carbon (ppmC)	StDev
1000 <sup>8</sup>	53.5	17.0
500 <sup>9</sup>	47.5	17.4
100 <sup>10</sup>	76.0	31.1

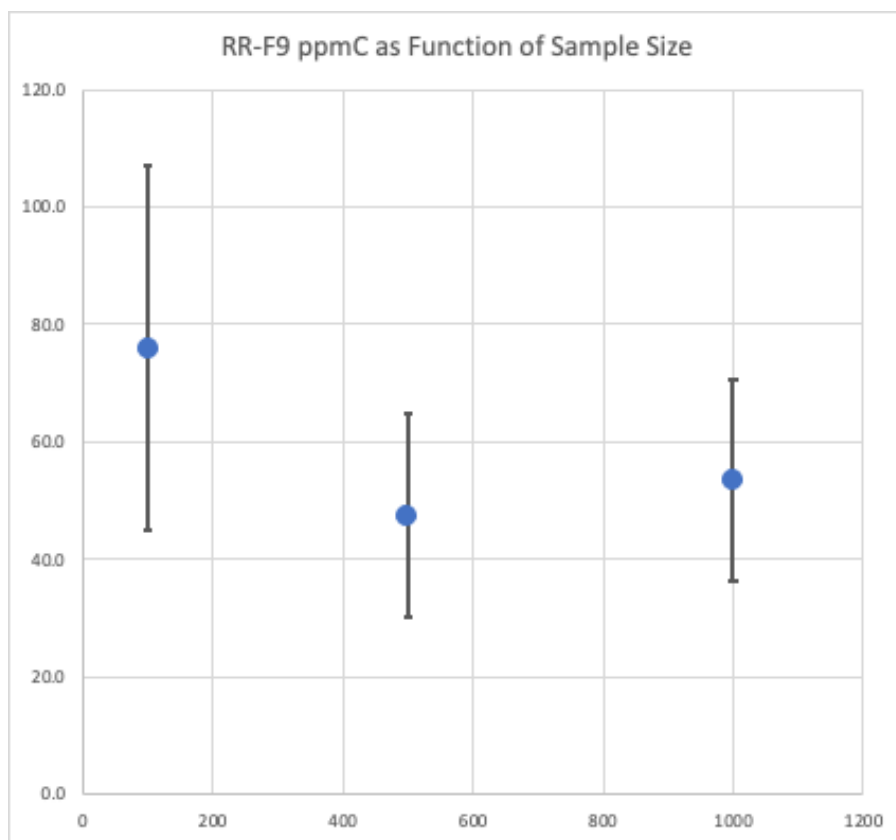


Figure 3: Natural Uranium Round Robin Lot F9 carbon content as a function of sample size

<sup>8</sup> Pages 113-114

<sup>9</sup> Page 114

<sup>10</sup> Pages 114-115

We added a variable into the sample size study of Lot D13. In addition to repeating the sample sizes we had previously used, we tried a “light flux” mix with the 100mg notional samples. We reduced the flux amounts to

0.5g W + 0.1g Sn + 100mg sample

in an attempt to have the flux:sample ratio more closely match the notional 1g tests. We were surprised to find that the “light flux” seemed to bring the averages back closer in line with the 1g sample results, but still not all the way.

RR-D13 Nominal Sample size (mg)	Average Carbon (ppmC)	StDev
1000 <sup>11</sup>	47.9	12.6
250 <sup>12</sup>	69.1	11.5
100 Standard Flux <sup>13</sup>	103.9	32.6
100 “Light Flux” <sup>14</sup>	72.5	48.6

---

<sup>11</sup> Page 112

<sup>12</sup> Pages 115-116

<sup>13</sup> Page 116

<sup>14</sup> Pages 117-118

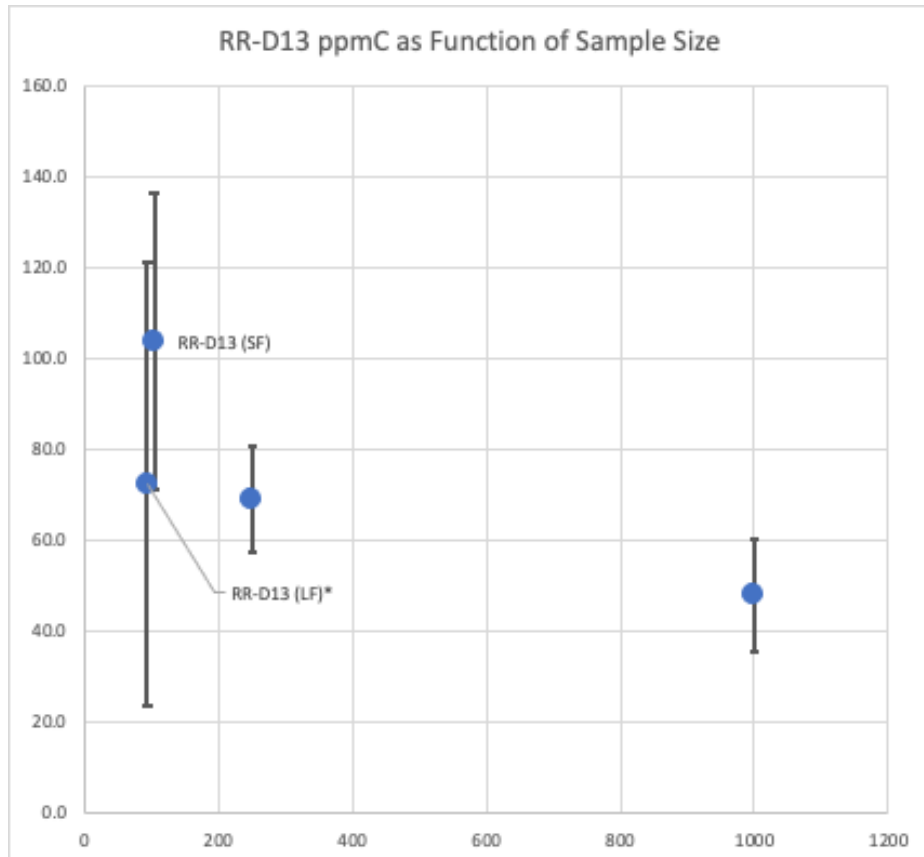


Figure 4: Natural Uranium Round Robin Lot D13 carbon content as a function of sample size. SF = Standard Flux. LF = Light Flux

### Unknown Steel Rod

More than a year after the main efforts on sample size, we apparently revisited the topic with a steel rod sample of unknown origin and carbon level. For the smaller samples, we again used the same “light flux” recipe described in the round robin analysis.

Steel Rod Nominal Sample size (mg)	Average Carbon (ppmC)	StDev
1000 <sup>15</sup>	348.3	7.0
500 <sup>16</sup>	357.5	7.3
250 “Light Flux” <sup>17</sup>	343.5	12.0
100 “Light Flux” <sup>18</sup>	330.3	12.1

<sup>15</sup> Pages 128-129

<sup>16</sup> Pages 129-130

<sup>17</sup> Page 130

<sup>18</sup> Pages 130-131

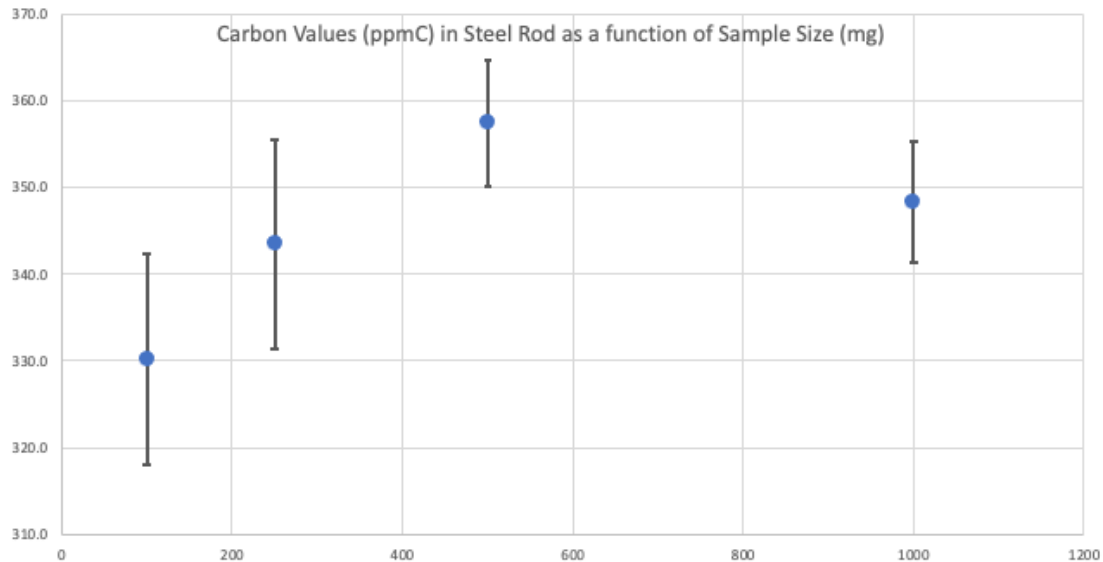


Figure 5: Unknown steel rod carbon content as a function of sample size

One interesting observation in this data set is that similar to the round robin samples, the light flux seems to reduce the measured value of carbon at lower sample sizes rather than raise it as seen in the previous uranium samples.

#### Granular Steel Standard

Not long after the steel rod analysis, we performed a sample size study using a commercial 370ppmC granular steel standard.<sup>19</sup>

In the first series, we used the standard flux recipe throughout the range of masses. Since the granular material was very easy to weigh, we were able to perform tests at more tightly spaced mass values. Previously we had seen that at some sample mass value, there is a deviation from the 1g sample average, and we were interested to see if we could determine a value for the breakover point that could help confirm our 500mg sample minimum protocol. Four samples at each mass were analyzed.

370ppmC granular steel standard-standard flux-Nominal Sample Size (mg)	Average Carbon (ppmC)	StDev
1000	356.1	2.0
750	363.6	4.6
500	378.2	8.0

<sup>19</sup> Pages 139-140

400	388.8	6.8
300	402.6	12.7
200	431.5	15.0
100	505.0	37.1
50	579.6	22.7

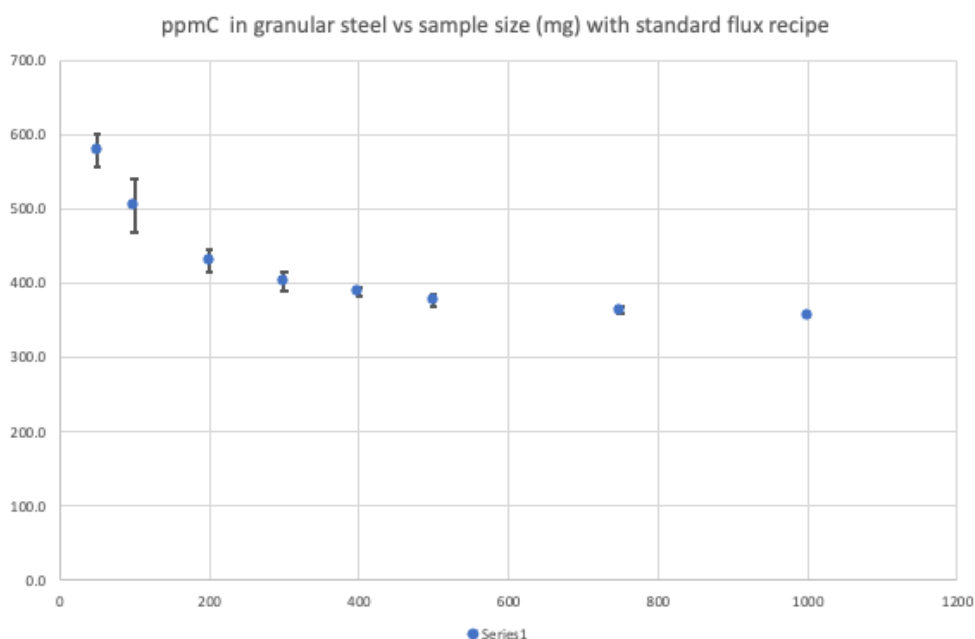


Figure 6: Commercial 370ppmC granular steel standard w/standard flux carbon content as a function of sample size

It appears once again, that there is a sample size effect on the results. The data suggest a deviation point somewhere between 400-500mg sample size.

Based upon the results with previous “light flux” analyses, we decided to perform the same sample size levels. As before, four samples were run for each mass.

370ppmC granular steel standard-“light” flux-Nominal Sample Size (mg)	Average Carbon (ppmC)	StDev
1000	343.1	1.9
500	355.6	7.2
400	357.4	4.8
300	345.7	12.1
200	328.4	20.8
100	300.0	12.5
50	174.2	29.7

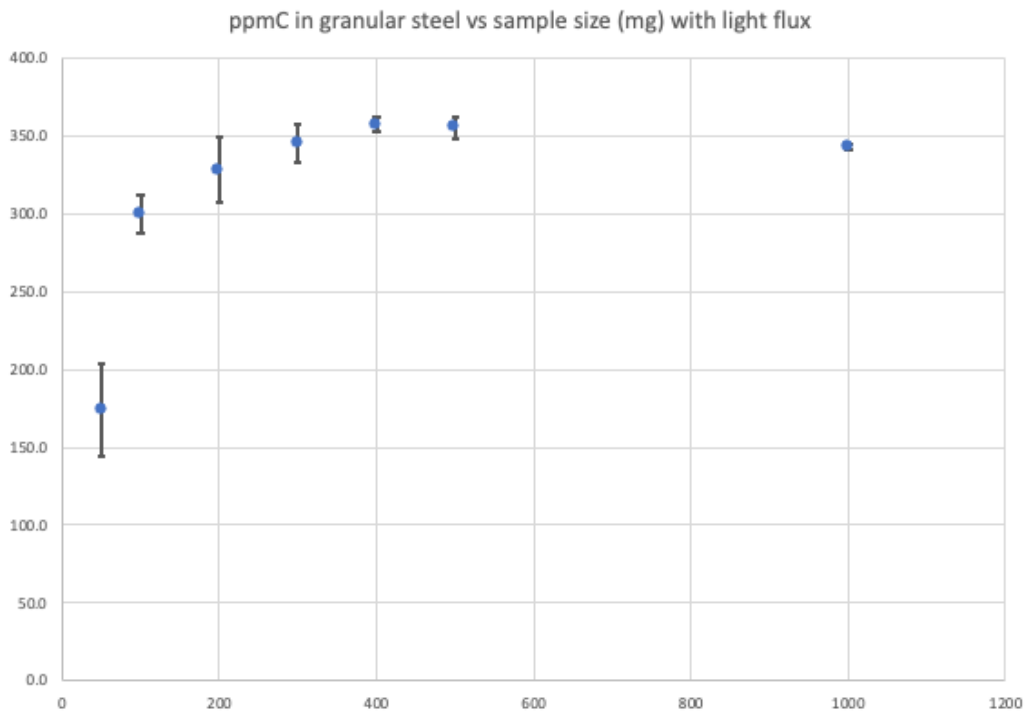


Figure 7: Commercial 370ppmC granular steel standard w/"light flux" carbon content as a function of sample size

With the "light flux," there appears to be a similar break point in the data that appears at approximately the same sample size (400-500mg) as the standard flux samples. What is curious is that with the "light flux" the deviation is in the opposite direction for all of the sample sets. We did not perform any additional tests to evaluate this result and leave it to future investigators to interrogate if desired.

The overall feeling at the end of all these studies was that our initial 500mg sample size was likely an appropriate minimum for consistent results from monolithic solid uranium samples.

#### Additional Data Sets Not Used

There was a sixth sample size study using 1g commercial 187ppmC steel pin standards cut in half (500mg nominal samples) and in thirds (333mg nominal samples)<sup>20</sup>. It is not clear that all these tests were performed with the same protocols and to the same rigor we had been using for the five sample size campaigns detailed above. We have chosen not to include them in this report.

<sup>20</sup> Pages 53-54, 54, 56-57, 57-58, 59-60

## Flux

- We established the following flux recipe standard based upon the manufacturer's operating manual and some experimental testing.

**1.5g W (tungsten) + 0.3g Sn (tin) + sample**

A fluxing agent (accelerant) is usually used to ensure complete melting and combustion of the sample. We retained the flux recipe and layering provided in the manufacturer's instruction manual for most of the samples we tested.

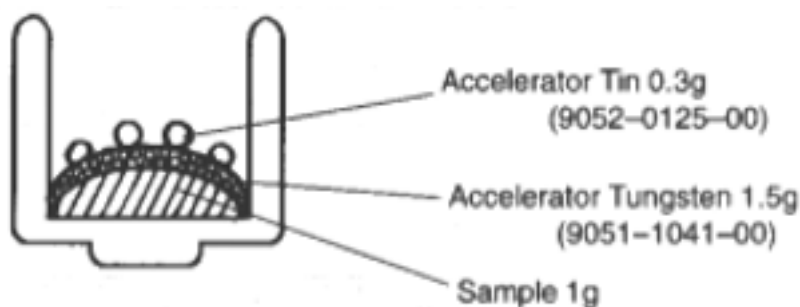


Figure 8: Flux recipe recommended in Horiba Instruction Manual <sup>21</sup>

We evaluated using a heavy flux load

**2.0g W + 0.5g Sn + 1g sample**

but found this caused unacceptable crucible boil-over and splattering on the inside of the furnace tube. We declined to use this mixture for any other samples.

We also tried using a “light flux” recipe, especially for smaller (<500mg) samples.

**0.5g W + 0.1g Sn + sample**

The results of these tests are detailed above. We generally did not use the “light flux” on any programmatic samples since we nearly always were able to analyze sample masses close to 1g.

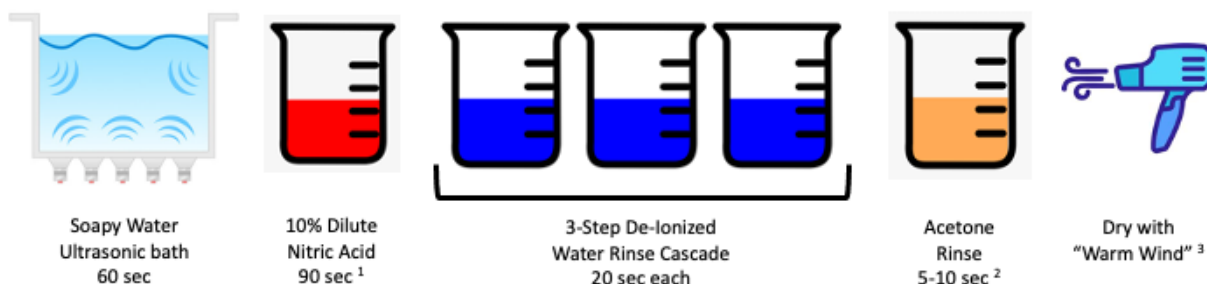
---

<sup>21</sup> Image taken from Horiba EMIA-8200W Instruction Manual, Second Edition, Horiba LTD, December 1997, Code I042935100, Page 51

## Sample Preparation

- We established the following sample preparation method based upon manufacturer's recommendations, experience at other facilities performing uranium carbon analysis, and our own evaluation tests.<sup>22</sup>

1. Ultrasonic bath in soapy water	60 sec
2. 10% dilute nitric acid	90 sec
3. De-ionized water rinse	20 sec
4. De-ionized water rinse	20 sec
5. De-ionized water rinse	20 sec
6. Acetone rinse	5-10 sec
7. Dry with "warm wind"	Visual check
8. Run analysis	As soon as possible



As with any chemical analysis, sample preparation is important to ensure no unintended carbon-containing material is analyzed and to remove any contaminants from the sample surface that might affect analytic results. This particular subject caused the most discussion within the DOE carbon analysis community.

During installation, the Horiba technician suggested that we use a dilute acid etch, a water rinse, and acetone or ethanol for drying. Since acetone contains carbon, the DOE community questioned whether or not the final drying rinse affected our carbon results. We used both a steel standard<sup>23</sup> and FSDrum-16 uranium samples to evaluate the effect of various cleaning, rinsing, and drying methods.

<sup>22</sup> In the image,

Note 1: A 5:1 Concentrated Nitric Acid cleaning for 15-20 seconds was also used on occasion

Note 2: If fully dried/evaporated from the sample surface, acetone was shown not to affect the carbon results

Note 3: This term was taken from one of the Horiba EMIA manuals. We utilized a standard commercial electric heat gun to dry the samples

<sup>23</sup> LECO catalog item 502-064 C in steel pin standard. 187ppmC +/- 7ppmC

Sample Condition	Average Carbon (ppmC)	StDev
Steel Pin Standard – as declared by LECO	187	7
Pin Standard - no cleaning <sup>24</sup>	179.0	3.8
pin standard Concentrated Nitric Acid clean (90 second soak) + 3-step De-Ionized water cascade rinse <sup>25</sup>	163.6	5.0
pin standard 10% dilute Nitric Acid clean (90 second soak) + 3-step De-Ionized water cascade rinse <sup>26</sup>	194.5	5.0
pin standard with no acid clean, instead used simple 3-step De-Ionized water cascade rinse <sup>27</sup>	192.4	3.5
pin standard with no acid clean or water rinse, instead cleaned with 5-10 second dip in acetone <sup>28</sup>	194.8	5.5
pin standard with no acid clean or water rinse, instead with long soak in acetone <sup>29</sup>	191.2	1.8
pin standard with no acid clean or water rinse, instead with 10 second dip in ethanol <sup>30</sup>	191.1	3.0
pin standard soaked in Trimsol (water soluble cutting oil used in DU machining) with no rinse. Some visual residual Trimsol could be seen on sample <sup>31</sup>	257.5	34.0
pin standard soaked in Trimsol (water soluble cutting oil used in DU machining) rinsed in an ultrasonic water bath <sup>32</sup>	199.0	4.8

Based on the results above, we felt comfortable the final acetone rinse did not affect the carbon results. Even with a short dip or a long soak in acetone, the carbon results are in line with the carbon levels of the certified standard. We believe that effectively no carbon remains on the surface of the sample after the acetone evaporated.

On the other hand, the need for appropriate cleaning is evident from the results of samples with residual cutting oils on the surface. This did not come as a surprise to us.

---

<sup>24</sup> Page 26

<sup>25</sup> Pages 26-27

<sup>26</sup> Page 28

<sup>27</sup> Page 29

<sup>28</sup> Page 30

<sup>29</sup> Page 31

<sup>30</sup> Pages 31-32

<sup>31</sup> Page 32

<sup>32</sup> Page 33

While acetone did not appear to affect the results on steel pins, we wanted to test the same method with uranium samples.

Sample Condition	Average Carbon (ppmC)	StDev
FSDrum-16 consolidated results	57.4	17.9
FSDrum16 1g samples, 10% dilute nitric acid clean (90 seconds) with 3-step De-Ionized water rinse (no acetone rinse) <sup>33</sup>	59.7	17.0
FSDrum16 1g samples, 10% dilute nitric acid clean (90 seconds) with 3-step De-Ionized water rinse, with acetone rinse <sup>34</sup>	62.4	9.9

As with the steel, it does not appear that a final acetone drying rinse affects carbon results in uranium. The DOE carbon analysis community concurred with our conclusion.

We did try some other sample preparation methods<sup>35</sup> but did not see any analytic benefit or other advantage over the fairly straightforward acid-rinse cascade protocol described here.

## Sample Morphology

Since monolithic solid samples were more easily available to us 20 years ago than they are today, we did little to evaluate the effect of sample morphology on carbon analysis results. There was concern at the time about how the increase in surface area and the challenge of adequately cleaning chip samples might impact repeatability and reliability of the measurements versus solid samples. There are a few places in the log book that indicate chip samples<sup>36</sup> were analyzed, and there is also one page of hand-written notes with results of cleaning and aging chips. Upon reflection, it is not clear that these results are adequately systematic or understood today at a level to provide insight or guidance to future analyses.

We suggest some investigation into sample morphology would likely be useful. We also think it may be useful to consider and evaluate using smaller flux:sample ratios if chip samples are significantly lower mass than the protocols we established herein.

---

<sup>33</sup> Pages 38, 42

<sup>34</sup> Pages 38, 42

<sup>35</sup> Including a 5V, 5sec, phosphoric acid electropolish, Page 39

<sup>36</sup> Pages 8-9, 13-14, 93, these runs may have been focused more on cleaning than accuracy